

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
28 March 2002 (28.03.2002)

PCT

(10) International Publication Number  
**WO 02/24446 A1**

- (51) International Patent Classification<sup>7</sup>: **B32B 27/04**, 29/06, B44C 5/04
- (21) International Application Number: PCT/US01/28140
- (22) International Filing Date:  
7 September 2001 (07.09.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
09/666,820 21 September 2000 (21.09.2000) US
- (71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).
- (72) Inventors: **CHANG, John, C.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). **FLETCHER, Edward, B.**; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).
- (74) Agents: **ALLEN, Gregory, D.** et al.; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EC, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
  - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
  - entirely in electronic form (except for this front page) and available upon request from the International Bureau
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 02/24446 A1**

(54) Title: ABRASION-RESISTANT LAMINATE

(57) Abstract: The present invention provides laminates, which may be high pressure or low pressure laminates, which include a base layer of cellulose fiber-based material impregnated with thermoset resin, a decorative sheet of paper impregnated with thermoset resin bonded to the base layer to provide a decorative surface to the laminate and hard mineral particles distributed over the decorative surface in the thermoset resin of the laminate to improve wear resistance. Specifically, at least a portion of the hard mineral particles comprised sol gel alpha alumina-based ceramic particles.

## ABRASION-RESISTANT LAMINATE

### Field of the Invention

The present invention relates to laminates and, more particularly, decorative  
5 laminates of high abrasion resistance because of the presence therein of hard particles  
comprising sol gel process alpha alumina-based ceramic particles.

### Background

High pressure decorative laminates have been typically produced by stacking and  
10 curing under heat and pressure a plurality of layers of paper impregnated with any of a  
variety of synthetic thermosetting resins which may be a phenolic resin, epoxy resin,  
polyester resin or polyurethane resin but commonly is an aminoplastic resin such as a  
melamine resin. Typically, the stacked assembly, from the bottom up, includes several  
core sheets made from phenolic resin impregnated kraft paper, above which is deployed  
15 one or more print sheets bearing a pattern impregnated with a thermoset resin such as an  
aminoplastic resin, e.g., a melamine resin. Frequently, superimposed on the print sheet is  
an overlay sheet which is almost transparent in the laminate to provide protection for the  
pattern of the print sheet.

The core sheets are typically made from kraft paper. Prior to stacking, the kraft  
20 paper is impregnated with a resin solution such as a water-alcohol solution of phenol-  
formaldehyde resole, dried and partially cured in a hot air oven, and finally cut into sheets.  
The print sheet typically is a high quality, pigment filled, alpha cellulose paper that has  
been impregnated with a resin solution such as a water-alcohol solution of melamine-  
formaldehyde resin, dried and partially cured, and finally cut into sheets. The print sheet,  
25 prior to impregnation with the resin solution, usually has been printed with a decorative  
design, or with a photogravure reproduction of natural materials, such as wood, marble,  
leather, etc.

The overlay sheet is frequently used when the print or pattern sheet has a surface  
image in order to protect the image from abrasive wear. The overlay sheet is typically a  
30 high quality alpha cellulose paper that is also typically impregnated with melamine-  
formaldehyde resin in a manner similar to that used for the print sheet, usually with a  
greater amount of resin per unit weight of paper. The individual sheets are stacked as

described above and, after lamination under heat and pressure, there results a finished laminate.

5 The stack of sheets as described above is placed between polished steel plates or other various textured surfaces and subjected to heat and pressure for a time sufficient to consolidate the laminate and cure the resins (typically between one to thirty minutes). This causes the resin in the paper sheets to flow, cure and consolidate the sheets into a unitary laminated mass referred to in the art as a high-pressure laminate.

10 At the completion of the laminating process, the back of the laminate is sanded and the laminate is adhered to a base such as particle board, plywood or other substrates. The laminate surfaced panel is then fabricated into any of a variety of products such as flooring, furniture, counter tops, table tops, wall panels, cabinets, tableware, store fixtures and other end-use applications.

15 One process of making such laminates is described in further detail in U.S. Pat. No. 4,327,141. There are many other variations in the process of making laminates described in the prior art. A number of variations of the above-described general process are known, particularly those operations designed to obtain special effects in appearance and texture.

20 Besides decorative high-pressure laminates referred to above, there are also a number of low-pressure products which have been developed, including low-pressure laminates using either saturated polyester resins, or melamine-formaldehyde resins which are normally pressed in a shorter cycle. These low-pressure products have the advantage of being less expensive, but they cannot be called "high pressure laminates" because in order to be entitled to that designation, a product must meet a variety of rigid standards established by the National Electric Manufacturers Association, NEMA LD3-1995 which includes specific standards relating to abrasive wear, stain resistance, heat resistance, impact resistance, dimensional stability, etc. While various other decorative printed, surfacing materials, such as some of the low-pressure laminates, have certain of the desirable characteristics, no products other than high-pressure laminates currently available have all of these properties.

30 One of these properties, in particular, which is very important in both high pressure laminates and low pressure laminates is wear resistance. High-pressure decorative laminates and low pressure decorative laminates must have sufficient wear resistance to

permit use in high use areas such as commercial dining table tops and check-out counters. The standard NEMA test for abrasion resistance in high pressure decorative laminates is NEMA test LD-3.13.

5 Poor wear resistance has been a long standing problem in the field of high pressure laminates. Many solutions to the problem have been suggested.

It is well known that small, hard mineral particles such as alumina dispersed in the overlay paper, or in resin mixtures to coat the impregnated pattern sheet, can enhance the abrasion resistance of high-pressure laminates. See, for example, U.S. Pat. Nos. 4,327,141; 5,344,704; 5,034,272; 4,940,503 and Re 30,233. Also see WO 97/00172,  
10 published January 3, 1997. While such additions of hard mineral particles have provided some degree of improved wear resistance in high pressure laminates there is a desire to provide a further improvement of wear resistance in such laminates.

It is also known to use sol gel process aluminum oxide grain in coating compositions which include film-forming resins to produce coatings exhibiting abrasion  
15 resistance, as described in WO 00/52105, published September 8, 2000. This reference does not, however, teach the preparation of either high pressure or low pressure laminates, nor does it disclose the unexpected nearly two-fold improvement in abrasion resistance, as provided by the present invention over laminates which include fused alumina particles as the hard mineral particles.

20

### **Summary of the Invention**

The present invention provides an improved abrasion-resistant laminate which has a higher degree of abrasion resistance than laminates which include fused alumina made according to the prior art. The improved laminate of the invention includes hard  
25 particulate mineral materials, as do certain laminates of the prior art, but at least a portion of the particulate mineral materials of the laminates of the present invention comprise sol gel alpha alumina-based ceramic particles. The laminate of the invention which includes sol gel alpha alumina-based ceramic particles in place of fused alumina particles has been found to have an unexpectedly higher degree of wear resistance because of the presence of  
30 the sol gel alpha alumina-based ceramic particles.

Specifically, the invention provides a laminate comprising:

- a. a base layer of cellulose fiber based material having a bottom surface and a top surface;
- b. a first thermoset resin impregnating the cellulose fiber based material;
- 5 c. a second thermoset resin overcoated on the top surface of the base layer; and
- d. sufficient hard mineral particles distributed over the top surface of the base layer in the second thermoset resin of the laminate to improve wear resistance in the top surface, wherein at least a portion of the hard mineral particles comprise sol gel alpha alumina-based ceramic particles.

10 In a further aspect, the invention provides a decorative thermoset laminate comprising:

- a. a base layer of cellulose fiber-based material impregnated with a first thermoset resin;
- b. a decorative sheet of paper impregnated with a second thermoset resin firmly
- 15 bonded to the base layer to provide a decorative surface to said laminate; and
- c. sufficient hard mineral particles distributed over the decorative surface in said second thermoset resin of said laminate to improve wear resistance in said decorative surface, wherein at least a portion of said hard mineral particles comprise sol gel alpha alumina-based ceramic particles.

20 The sol gel alpha alumina-based ceramic particles may comprise up to 100% by weight of the hard mineral particles included in the claimed decorative thermoset laminate to improve wear resistance. Improvements in performance are noted if at about 10% - 50% by weight of the hard mineral particles are sol gel alpha alumina-based ceramic particles. The remainder of the hard mineral particles in the laminate to provide wear

25 resistance may comprise any other material such as fused alumina, silicon carbide, silica and any other hard material, preferably possessing a Moh's hardness of at least 7.

The average particle size range of the hard mineral particles in the decorative laminate to improve wear resistance is in the range of about 5 to 70 micrometers, preferably about 10 to 50 micrometers.

30 The particle size distribution of the hard mineral particles contained in the laminate may comprise hard particles having a first average particle size and at least one other average particle size. For example, the first average particle size could be a smaller

average particle size such as 10 micrometers and the second average particle size could be a larger particle size such as 50 micrometers. Such a particle size distribution is thought to provide improved wear performance in the claimed decorative laminate.

5 The laminate may be a high pressure laminate or a low pressure laminate, as described above. The first thermoset resin and the second thermoset resin may be of the same composition.

### **Detailed Description**

10 The processes utilized for making the claimed laminate of the present invention are conventional processes for making such products. The details of these processes may be found in any of a variety of prior art references dealing with this subject. Several of these references have previously been cited and are incorporated herein by reference. The process steps for including hard particulate mineral materials in such laminates is also adequately described in the prior art. The particulate material may be blended into the  
15 uncured binder which is then coated on the pattern sheet (or overlay sheet, if used) or may be sprinkled on a coating of uncured binder to provide a uniform pattern of particles.

The present invention involves the selection of a particular type of hard mineral product to include in the claimed laminates to give improved performance. The particular material which provides this improved performance is a sol gel process alpha alumina-based ceramic particulate material. The term "sol gel alpha alumina-based ceramic" as  
20 used herein refers to ceramic materials that were made by a sol gel process, as described below. Such ceramic materials may comprise 100% alpha alumina or they may be mainly alpha alumina with various metal oxide modifiers; thus, they are "alpha alumina-based." They are ceramic materials which are sintered and have not been subjected to melt  
25 temperatures of alumina. Such sol gel ceramic particulate materials are also known in the prior art. These materials are made according to any of U.S. Pat. Nos. 4,314,827; 4,744,802; 4,770,671; 4,881,951; 5,453,140; and 5,752,996. The sol gel alpha alumina-based ceramic particles may also be made according to U.S. Pat. No. 4,623,364.

### **30 Dispersion Preparation**

The first step to make the sol gel alpha alumina-based ceramic particles is to prepare a dispersion that comprises an alumina precursor, optional containing acid, in a

liquid medium such as water. The alumina precursor in the dispersion is capable of being sintered to provide alpha alumina crystalline particles. The preferred alumina precursor is alpha alumina monohydrate, commonly referred to as boehmite. Examples of other alumina precursors include alpha alumina powders, gamma alumina powders, aluminum formoacetate, aluminum nitroformoacetate and aluminum salts.

Useful alpha alumina monohydrate for this invention is commercially available. One supplier of alpha alumina monohydrate is Alcoa Company. Other sources of alpha alumina monohydrate include that commercially available from Condea Chemie GmbH, Hamburg, Germany under the trade designations of "DISPERSAL" and from Vista Chemical Company under the trade designation "CATAPAL". The alumina monohydrates are typically in the alpha form, and include relatively little, if any, hydrated phases other than monohydrates (although very small amounts of trihydrate impurities may be present in some commercial grade boehmite, which can be tolerated). The alumina monohydrates have a low solubility in water and have a high surface area (typically at least about 180 m<sup>2</sup>/g).

The liquid medium in which the boehmite is dispersed is typically water. The water may be tap water, distilled water or deionized water. It is sometimes preferable to heat the aqueous medium (at, e.g., 30-70°C) to improve the dispersibility of the boehmite.

The dispersion may further comprise a peptizing agent, generally one or more soluble ionic compounds, to cause the surface of a particle or colloid to be uniformly charged in the aqueous medium. The preferred peptizing agents are acids or acid compounds. Examples of useful acids include monoprotic acids and acid compounds, such as acetic, hydrochloric, formic and nitric acid, with nitric acid being preferred. Typically, the dispersion contains at least, 0.1 to 20%, preferably 1% to 10% by weight acid and most preferably 3 to 8% by weight acid, based on the weight of boehmite in the dispersion. In some instances, the acid may be applied to the surface of the alpha alumina monohydrate particles prior to being combined with the water.

The dispersion may further comprise a nucleating material or nucleating material precursor such as alpha alumina, alpha iron oxide, an alpha iron oxide precursor and/or chromia. Additional details regarding nucleating materials are disclosed, for example, in U.S. Pat. Nos. 4,623,364 (Cottringer et al.), 4,744,802 (Schwabel), 4,964,883 (Morris et al.), 5,139,978 (Wood), and 5,219,806 (Wood). An example of a nucleating material is

iron oxide or an iron oxide precursor. Sources of iron oxide, which in some cases may act as or provide a material that acts as a nucleating material, include hematite (i.e.,  $\alpha\text{-Fe}_2\text{O}_3$ ), as well as precursors thereof i.e., goethite ( $\alpha\text{-FeOOH}$ ), lepidocrocite ( $\gamma\text{-FeOOH}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ).

5        The alumina dispersion may further comprise other metal oxide precursors, sometimes referred to as a metal oxide modifier. The term precursor means that the material is capable of being converted to metal oxide under appropriate sintering conditions. The amount of the metal oxide precursor added to the dispersion is calculated and determined based upon the desired amount in the final fired mineral particle. The  
10       other metal oxides may alter the physical properties and/or chemical properties of the resulting mineral particle. The metal oxide precursor may be added to the dispersion as, for example, a metal salt, a metal oxide particle or a colloidal suspension of the metal oxide. The preferred method of addition is to add the precursor by the metal salt approach and examples of additive metal salts include metal nitrate salts, metal acetate salts, metal  
15       citrate salts, metal formate salts, and metal chloride salts. For metal oxide particles, it is generally preferred that the metal oxide particles are generally of an average particle size less than 5 micrometers, preferably less than 1 micrometer. The colloidal metal oxides are discrete finely divided particles of amorphous or crystalline metal oxide having one or more of their dimensions within a range of about 3 nanometers to about 1 micrometer.  
20       Examples of these metal oxides include, for example, lithium oxide, manganese oxide, zirconium oxide, silica, chromium oxide, praseodymium oxide, dysprosium oxide, samarium oxide, cobalt oxide, zinc oxide, neodymium oxide, yttrium oxide, ytterbium oxide, magnesium oxide, nickel oxide, silica, manganese oxide, lanthanum oxide, gadolinium oxide, dysprosium oxide, europium oxide, ferric oxide, hafnium oxide, and  
25       erbium oxide.

Typically, the use of a metal oxide modifier can decrease the porosity of the sintered mineral particle and thereby increase its density. Additionally, certain metal oxide precursors may reduce the temperature at which the transitional alumina phases transform into alpha alumina. Certain metal oxides may react with the alumina to form a  
30       reaction product and/or form crystalline phases with the alpha alumina which may be beneficial in enhancing the physical properties of the mineral particle. Thus, the selection



and amount of metal oxide will depend in part upon the processing conditions and the desired frictional properties of the mineral particle.

5 The oxides of cobalt, nickel, zinc, and magnesium typically react with alumina to form a spinel, whereas zirconia and hafnia do not react with the alumina. Alternatively, the reaction products of dysprosium oxide and gadolinium oxide with aluminum oxide are generally garnet. The reaction products of praseodymium oxide, ytterbium oxide, erbium oxide, and samarium oxide with aluminum oxide generally have a perovskite and/or garnet structure. Ytria can also react with the alumina to form  $Y_3Al_5O_{12}$  having a garnet crystal structure. Certain rare earth oxides and divalent metal cations react with alumina to form  
10 a rare earth aluminate represented by the formula  $LnMAl_{11}O_{19}$ , wherein Ln is a trivalent metal ion such as  $La^{3+}$ ,  $Nd^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Sm^{3+}$ ,  $Gd^{3+}$ ,  $Er^{3+}$ , or  $Eu^{3+}$ , and M is a divalent metal cation such as  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ , or  $Co^{2+}$ . Such aluminates have a hexagonal crystal structure and are sometimes referred to as a magnetoplumbite platelet. For additional details regarding the inclusion of metal oxide (and/or precursors thereof) in a  
15 boehmite dispersion, see, for example, U.S. Pat. Nos. 4,314,827 (Leitheiser et al.), 4,770,671 (Monroe et al.), 4,881,951 (Wood et al.) 5,429,647 (Larmie), and 5,551,963 (Larmie).

The alumina based dispersion typically comprises greater than 15% by weight (generally from greater than 30% to about 80% by weight) solids, based on the total  
20 weight of the dispersion. Certain dispersions, however, comprise 35% by weight or more, 45% by weight or more, 50% by weight or more, 55% by weight or more, 60% by weight or more and 65% by weight or more by weight or more solids, based on the total weight of the dispersion.

The dispersion may be prepared, for example, by gradually adding one or more  
25 liquid components to one or more components that are not soluble in the liquid components, while the latter is mixing or tumbling. For example, a liquid containing water, nitric acid, and metal salt may be gradually added to boehmite, while the latter is being tumbled such that the liquid is more easily distributed throughout the boehmite. Alternatively, the dispersion may be formed by combining boehmite, water and acid and  
30 then mixed to form essentially a homogeneous dispersion. Next, nucleating agents and/or metal oxide precursors may be added to the dispersion.

Suitable mixers include pail mixers, sigma blade mixers, ball mill and high shear mixers. Other suitable mixers may be available from Eirich Machines, Inc. of Gurnee, IL; Hosokawa-Bepex Corp. of Minneapolis, MN (including a mixer available under the trade designation "SCHUGI FLEX-O-MIX", Model FX-160); and Littleford-Day, Inc. of Florence, KY.

After the alumina based dispersion is formed, the dispersion may be heated to increase the dispersibility of the alpha alumina monohydrate and/or to create a homogeneous dispersion. The temperature may vary to convenience, for example the temperature may range from about 20 to 80° C., usually from about 25 to 75° C.

Alternatively, the dispersion may be heated under a pressure ranging from 1.5 to 130 atmospheres.

The dispersion may gel prior to or during the drying step. The addition of most modifiers may result in the dispersion gelling faster. The pH of the dispersion and concentration of ions in the gel generally determines how fast the dispersion gels.

Typically, the pH of the dispersion is within a range of about 1.5 to about 4. A gelled dispersion may be extruded to provide shaped structures which are more easily handled during drying.

### **Drying Step**

In general, techniques for drying the dispersion are known in the art, including heating to promote evaporation of the liquid medium, or simply drying in air. The drying step generally removes a significant portion of the liquid medium from the dispersion; however, there still may remain a minor portion (e.g., about 10% or less by weight based on dried solids) of the liquid medium present in the dried dispersion. Typical drying conditions include temperatures ranging from about room temperature to over about 200° C, typically the temperature range is between 50 to 150° C. The drying times may range from about 30 minutes to several days.

### **Converting Dried Dispersion into Precursor Particles**

After drying, the dried dispersion may be converted into precursor particles. One typical means to generate precursor particles is by a crushing technique. Various crushing or comminuting techniques may be employed such as a roll crusher, jaw crusher, hammer

mill, ball mill and the like. Coarser precursor particles may be recrushed to generate finer particles.

Alternatively, the dried dispersion may be shaped into lumps with a high volatilizable content which then are explosively comminuted by feeding the lumps directly into a furnace held at a temperature above 350° C, usually a temperature between 600 to 900° C.

### Calcining Step

In general, techniques for calcining the dried dispersion or ceramic precursor material, wherein essentially all the volatiles are removed, and the various components that were present in the dispersion are transformed into oxides, are known in the art. Such techniques include using a rotary or static furnace to heat dried dispersion particles at temperatures ranging from about 400-1000° C (typically from about 450-800° C) until any free water, and up to about 90 percent by weight of any bound volatiles are removed.

### Impregnation Steps

The metal oxide modifier precursor described above may be impregnated into a calcined precursor particle, although the impregnation process is not required. For example, a zirconium salt may be impregnated into the calcined precursor particle to provide the improved characteristics in the mineral particle. Methods of impregnating sol gel derived particles are described in general, for example, in U.S. Pat. No. 5,164,348 (Wood). In general, ceramic precursor material (i.e., dried alumina-based dispersion (or dried ceramic precursor material), or calcined alumina-based dispersion (or calcined ceramic precursor material)) is porous. For example, a calcined ceramic precursor material typically has pores about 5-10 nanometers in diameter extending therein from an outer surface. The presence of such pores allows an impregnation composition in the form of a mixture comprising the liquid medium (typically water) and an appropriate metal precursor to enter into porous precursor material. The metal salt material is dissolved in a liquid, and the resulting solution mixed with the porous precursor particle material. The impregnation process is thought to occur through capillary action.

The liquid used for the impregnating composition is preferably water (e.g., deionized water), an organic solvent (preferably a non-polar solvent), or mixtures thereof.

If impregnation of a metal salt is desired, the concentration of the metal salt in the liquid medium is typically in the range from about 5% to about 40% dissolved solids, on a theoretical metal oxide basis. Preferably, there is at least 50 ml of solution added to achieve impregnation of 100 grams of porous precursor particulate material.

- 5           After the impregnation step, the resulting impregnated precursor particle is typically calcined a second time to remove any volatiles prior to sintering. The conditions for this second calcining step are described above.

### **Sintering**

- 10           After the precursor particle is formed or optionally calcined, the precursor particle is sintered to provide a dense ceramic alpha alumina-based mineral particle. In general, techniques for sintering the calcined material, which include heating at a temperature effective to transform transitional alumina(s) into alpha alumina, to cause all of the metal oxide precursors to either react with the alumina or to form metal oxide, and increasing the
- 15           density of the ceramic material, are known in the art. The calcined material may be sintered by heating (e.g., using electrical resistance, microwave, plasma, laser, or gas combustion, on batch basis or on a continuous basis. The sintering temperatures will usually range from about 1200°C to about 1650°C, typically, from about 1200°C to about 1500°C. The length of time which the calcined material is exposed to the sintering
- 20           temperature depends, for example, on particle size, composition of the particles, and sintering temperature. Typically, sintering times may range from a few seconds to about 60 minutes, but preferably is within about 3-30 minutes. Sintering is typically accomplished in an oxidizing atmosphere, although neutral or reducing atmospheres may also be useful.

25

### **Crushing and Classification Process**

- In some instances, the mineral particle is sintered to about the desired particle size and about the desired particle size distribution. The mineral particle may be further classified using screening techniques, air classification techniques or water classification
- 30           techniques to further refine the particle size distribution. If the mineral particles are too "large" in size, they may be first crushed to smaller particle size distribution. Crushing may be accomplished, for example, by roll crushing, jet milling, hammer milling, ball

milling and the like. After crushing, the resulting ceramic particles are typically classified using screening techniques, air classification techniques or water classification techniques to further refine the particle size distribution.

## 5 Sintered Alumina Mineral Particle

The sintered alumina mineral particle comprises alpha alumina crystals as a dense alumina body. The alpha alumina crystals are typically less than 15 micrometers in average crystal size, preferably less than 10 micrometers in average crystal size, more preferably less than 5 micrometers in average crystal size and most preferably less than about 3 micrometers in average crystal size. The crystal sizes are usually measured by any conventional technique such as by use of a scanning electron microscope or a transmission electron microscope.

Some of the sintered mineral particles may comprise alpha alumina crystals ranging in size from about 2 to 5 micrometers having therebetween magnetoplumbite platelets which reinforce the alpha alumina crystals and are usually composed of:  $\text{LnMA}_{11}\text{O}_{19}$ , wherein Ln is a trivalent metal ion such as  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Er}^{3+}$ , or  $\text{Eu}^{3+}$ , and M is a divalent metal cation such as  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ , or  $\text{Co}^{2+}$ . These platelets typically have a length ranging from about 0.5 to about 2.0 micrometers, typically between about 0.8 to about 1.2 micrometer and a width ranging from about 0.05 to about 1.0 micrometer, typically from about 0.1 to 0.5 micrometer.

Some of the sintered particles comprise alpha alumina crystals ranging in size from about 0.1 to 1.0 micrometer, typically from about 0.1 to 0.5 micrometer. It is preferred that essentially all of the alpha alumina crystals have a crystal size less than 0.6 micrometer.

The sintered alumina mineral particle typically has a true density of at least about 3.70 grams/cm<sup>3</sup>, preferably at least about 3.80 grams/cm<sup>3</sup>, more preferably at least about 3.85 grams/cm<sup>3</sup>, and most preferably at least about 3.90 grams/cm<sup>3</sup>. Likewise, it is preferred that the sintered alumina mineral particle have a theoretical density of at least about 90%, preferably at least about 93% and more preferably at least about 95%. The densities of the abrasive grain for the may be determined with a helium gas pycnometer (available under the trade designation "Micromeritics AccuPyc 1330" from Micromeritics Instruments Corp., Norcross, Ga.).

The sintered alumina mineral particle typically has a hardness of at least about 16 GPa, preferably at least about 17 GPa, more preferably at least about 18 GPa and most preferably at least about 19 GPa. In some instances, the hardness may be greater than about 20 GPa or greater than about 22 GPa. The hardness may be measured according to a Vicker's indentation method using a 500 gram load. This test procedure is further described in accordance with ASTM (American Society of Testing Methods) Test Method E384.

The sintered alumina mineral particle typically has a toughness of at least about 2 MPa·m<sup>0.5</sup>, preferably at least about 2.2 MPa·m<sup>0.5</sup>, more preferably at least about 2.5 MPa·m<sup>0.5</sup>, and most preferably at least about 2.8 MPa·m<sup>0.5</sup>. In some instances, the toughness may be greater than about 3.0 MPa·m<sup>0.5</sup>, or greater than about 4.0 MPa·m<sup>0.5</sup>. The toughness may be measured according to a Vicker's indentation method using a 500 gram load. The toughness may be measured according to a test procedure outlined in the article "Equilibrium Penny-Like Cracks in Indentation Fracture" authored by BR Lawn and ER Fuller published in the Journal of Material Science, Volume 10, 1974 pages 2016-2024.

The sol gel alpha alumina-based ceramic particles that are useful in preparing the laminates of the present invention are commercially available from Minnesota Mining and Manufacturing Company, St. Paul, MN, under the trade designation Cubitron™ 321 abrasive grain. Useful sizes for use in this invention preferably include that having a particle size on the order of JIS grade 220, or finer, such as JIS grade 400, having an average particle size of  $34 \pm 2$  micrometers.

A further advantage of the invention is that the amount of hard particulate material may be reduced because of the presence of the sol gel derived alpha alumina-based ceramic particulate material. Typically, amounts of hard particulate material in the topical protective layer of the laminate has been on the order of 2 to 15 weight percent or higher based on the solids content of the thermoset resin. Because the sol gel alpha alumina-based ceramic material is more durable than conventional mineral particulate materials such as fused alumina, less of the sol gel derived alpha alumina-based ceramic material will be needed to provide the desired wear resistance in the laminate. Further, the larger amount of conventional particulate material in the protective layer of the laminate tends to cause some undesirable hazing which may obstruct the image of the decorative layer of

the laminate. Such hazing may be avoided by use of smaller quantities of the sol gel derived alpha alumina-based ceramic particulate material.

The amount of sol gel alpha alumina-based ceramic particles in the topical protective layer may vary, depending on the desired result. The amount may be as little as 0.5% by weight, based on the dry weight of the thermoset resin of the protective layer, up to as much as 25% by weight. Amounts outside this range may also be useful. Where blends of sol gel alpha alumina-based ceramic particles are used with other hard mineral particles, the amount would be lower. A suitable blending mineral would be, for example, fused alumina.

As previously mentioned, the laminates of the present invention are made by following conventional process steps. The laminate of the invention may include the overlay sheet or the overlay sheet may be omitted, depending upon the particular construction involved. Further, the laminate may include a paper pattern sheet or not. In the case where no pattern sheet and no overlay sheet is included in the laminate, the hard mineral particles are merely distributed evenly over the top surface of the base layer in the thermoset resin to provide a wear resistant surface.

The thermosetting resins are conventional resins that are commercially available. A commercially available water-based melamine-formaldehyde condensate solution which is useful in practicing the invention is available under the trade designation Resimene™ AG-7550 from Solutia, Inc., St. Louis, MO as a 78 percent by weight solids solution. This resin is cured under conventional conditions in presence of catalyst that are well known in the laminate producing art. Catalysts such as p-toluenesulfonic acid and sulfuric acid at a level of about 0.05 to 1 weight percent are frequently used, based on the solids in the resin solution.

The paper employed in the laminate is also a conventional material that is typically employed in making laminates. For example, a 21 pound per ream (a ream being 3,000 square feet) (13.6 kg per 278.7 m<sup>2</sup>) outer popcorn raw stock paper having a Gurley porosity of 125 seconds obtained from International Paper Company, Purchase, NY, is a suitable paper.

The hard particles comprised of sol gel alpha alumina-based ceramic material are typically introduced in the protective coating as it is applied to the laminate, either on the overlay sheet, if it is used, or on the pattern sheet, if no overlay sheet is used. The

particles are typically dispersed in the resin solution to obtain a uniform dispersion of the particles and the solution containing the dispersed particles is coated on the laminate by employing conventional techniques. Suitable coating techniques include roll coating, Meyer bar coating, curtain coating, extrusion coating, spray coating and the like. In some cases the particles may simply be drop coated, electrostatic coated, or sprinkled over a wet coating of binder to provide a uniform distribution of particles. The particle loaded coating may then be overcoated with additional binder followed by curing.

Curing the laminate is also by conventional well known techniques. Curing typically takes place between polished steel plates under heat and pressure for a time sufficient to consolidate the laminate and cure the resins. This causes the resin in the paper sheets to flow, cure and consolidate the sheets into a unitary laminated mass to produce the laminate.

#### **Examples**

The following examples, wherein all parts and percentages are by weight, unless otherwise specified, further illustrate the claimed invention.

Three examples are provided, two control examples and four according to the invention. The laminates described in the examples are made on a laboratory scale for illustrative purposes to show the benefits of including the sol gel alpha alumina-based ceramic particles in the laminate. Control Example A contains no hard particles to improve wear resistance. Control Example B is offered as an illustration of the state of the art which typically utilizes fused alumina particles in the laminate to improve wear resistance. Examples 1 – 4 show the benefit of substituting the fused alumina particles with sol gel alpha alumina-based ceramic particles.

#### **Ingredients**

Cubitron™ 321 mineral, JIS grade 400 sol gel-derived, alpha alumina-based ceramic particles having an average particle size of  $34 \pm 2$  micrometers obtained from Minnesota Mining and Manufacturing Company, St. Paul, MN.

Alodur™ mineral, P400 grade fused brown alumina particles having an average particle size of  $35 \pm 1.5$  micrometers obtained from Treibacher Schleifmittel AG, Austria.



Resimene™ AG-7550, 78% by weight solids water-based melamine-formaldehyde condensate solution obtained from Solutia, Inc., St. Louis, MO.

Catalyst, p-toluenesulfonic acid.

5 Paper, 21 pound (13.6 kg) per ream (3,000 square feet) (278.7m<sup>2</sup>) outer popcorn raw stock paper having a Gurley porosity of 125 seconds obtained from International Paper, Inc., Purchase, NY.

#### **Control Example A**

10 A 5 inch (12.7 cm) by 12 inch (30.5 cm) sheet of paper weighing 34 grams per square meter (gsm) was dip-coated with the Resimene™ AG-7550 solution that had been diluted to 39% solids with DI water, resulting in a 125% wet add-on weight. The wet paper was placed on a glass plate and coated on one side with the concentrated (78% solids) Resimene™ AG-7550 solution with a #40 Meyer bar coater. Each Resimene™ AG-7550 solution contained 0.5 weight percent of p-toluenesulfonic acid catalyst based on  
15 resin solids. The coated paper sheet was then suspended horizontally on a metal frame and dried in a forced air oven at 110° C. for 6 minutes. The dry, coated sheet was weighed and the resin add-on of 141% solids was calculated based on the original weight of paper. Three identical coated sheets prepared as described above were laminated between heated polished steel plates under 1185 psi (83.3 kg/cm<sup>2</sup>) for 4 minutes at 150° C. No hard  
20 particles were added to the concentrate solution of Resimene™ AG-7550.

#### **Control Example B**

Control Example B was prepared in an identical manner as Control Example A except 7 weight percent of Alodur™ EPL fused alumina particles was added to the  
25 concentrate Resimene™ AG-7550 solution before coating. The mixture was stirred by hand before coating to evenly distribute the particles.

#### **Example 1**

Example 1 was prepared in an identical manner as Control Example B except  
30 Cubitron™ 321 sol gel alpha alumina-based ceramic particles were used at 7 weight percent in place of the Alodur™ EPL fused alumina particles.

**Example 2**

Example 2 was prepared in an identical manner as Example 1 except 3.5 weight percent of Cubitron™ 321 sol gel alpha alumina-based ceramic were used as in Example 1.

5

**Example 3**

Example 3 was prepared in an identical manner as Example 1 except 3.5 weight percent of Cubitron™ 321 sol gel alpha alumina-based ceramic particles and 3.5 weight percent of the Alodur™ EPL fused alumina particles mixture were used as in Example 1.

10

**Example 4**

Example 4 was prepared in an identical manner as Example 1 except 0.7 weight percent of Cubitron™ 321 sol gel alpha alumina-based ceramic particles and 6.3 weight percent of the Alodur™ EPL fused alumina particles mixture were used as in Example 1.

15

**Testing**

Each Example was done in duplicate and the test results reported are the average of tests performed on the 2 samples of each Example.

Each laminate was adhered to a 4 inch (10 cm) diameter 1/16 inch (0.16 cm) thick polycarbonate disc with a ¼ inch (0.6 cm) center hole using double-sided pressure sensitive adhesive tape obtained from the 3M Company. The laminate/disc assembly was then pressed using a Carver Laboratory Press Model 2625 obtained from Fred S. Carver, Inc. under 1,000 psi (70.3 kg/cm<sup>2</sup>) at room temperature for 6 minutes to produce flat specimens for the abrasion test. The laminates were then edge trimmed to provide 4 inch (10 cm) diameter discs.

25

Testing was done on a Taber™ Abraser™ Abrasion Testing Device Model 5150 obtained from Taber Industries, Inc. Wear resistance was measured according to NEMA standard test method LD-3-1995, 3-13, using 180 grit sandpaper except the measurement guidelines were not followed. Instead, the initial weight of each sample was recorded and subsequent weights were taken respectively after abrasion cycles of 500, 1,000, 1,500, 2,000, 2,500 and 3,000. The number of cycles to wear through was also recorded. The results are reported in the following Table.

30

**Table 1**

Example Number	Control A	Control B	1
Hard Particles	none	fused alumina	Sol gel ceramic
Taber Abrasion Cycles	Wt. Loss	Wt. Loss	Wt. Loss
	(grams)	(grams)	(grams)
500	0.4593	0.1328	0.0198
1,000	Failed	0.1921	0.0449
1,500	-	0.2985	0.0758
2,000	-	0.4005	0.1287
2,500	-	0.4676	0.2197
3,000	-	0.5320	0.2783
Cycles to wear through	<1,000	3518	7002

- 5 The comparative test results illustrate the advantage of this invention. The laminate with Cubitron™ mineral particles in Example 1 showed a 91% improvement in weight loss after abrasion when compared with the laminate made with fused alumina in Control Example B, and an even greater improvement was demonstrated over the control in Control Example A, which contained no mineral particles. It took about twice the number of Taber abrasion cycles to wear through the laminate layer with Cubitron™ particles than the comparative laminate with fused alumina particles.

**Table 2**

Example Number	Control B	2	3	4
Hard Particles	fused alumina	Sol gel ceramic	Sol gel ceramic and fused alumina	Sol gel ceramic and fused alumina
Weight Ratio, Sol gel ceramic/fused alumina	0/100	100/0	50/50	10/90
Weight % of particles used	7	3.5	7	7
Taber Abrasion Cycles	Wt. Loss	Wt. Loss	Wt. Loss	Wt. Loss
	(grams)	(grams)	(grams)	(grams)
500	0.1328	0.0233	0.0187	0.0185
1,000	0.1921	0.0577	0.0494	0.0508
1,500	0.2985	0.1805	0.1458	0.1256
2,000	0.4005	0.2831	0.2514	0.2263
2,500	0.4676	0.3568	0.3090	0.3078
3,000	0.5320	0.4436	0.3485	0.3503

The laminate with Cubitron™ mineral particles in Example 2 showed a lower weight loss than the Control Example B after 3,000 abrasion cycles when only a half amount of mineral particles were used. Laminates with Cubitron™ mineral particles in Example 3 and 4 showed improvements in performance when only a fraction of the hard mineral particles are sol gel alpha alumina-based ceramic particles compared with the Control Example B after 3,000 abrasion cycles.

As understood by those skilled in the art, various modifications and changes may be made in the invention without departing from the spirit and scope of the invention. The embodiments of the invention disclosed herein are merely illustrative of the various modifications that the invention may have and they are not intended to limit the scope of the invention.

What is claimed is

1. A decorative thermoset laminate comprising:
  - a. a base layer of cellulose fiber-based material impregnated with a first thermoset resin;
  - b. a decorative sheet of paper impregnated with a second thermoset resin firmly bonded to the base layer to provide a decorative surface to said laminate; and
  - c. sufficient hard mineral particles distributed over the decorative surface in said second thermoset resin of said laminate to improve wear resistance in said decorative surface, wherein at least a portion of said hard mineral particles comprise sol gel alpha alumina-based ceramic particles.
2. The decorative laminate of claim 1 wherein said sol gel alpha alumina-based ceramic particles comprise up to 100% by weight of said hard mineral particles.
3. The decorative laminate of claim 1 wherein said sol gel alpha alumina-based ceramic particles comprise at least 50% by weight of said hard mineral particles.
4. The decorative laminate of claim 1 wherein said sol gel alpha alumina-based ceramic particles comprise at least 10% by weight of said hard mineral particles.
5. The decorative laminate of claim 1 wherein said hard mineral particles comprise a mixture of sol gel alpha alumina-based ceramic particles and hard mineral particles made of another material.
6. The decorative laminate of claim 5 wherein said another material is fused alumina.
7. The decorative laminate of claim 1 wherein said hard mineral particles have an average particle size in the range of about 5 to 70 micrometers.
8. The decorative laminate of claim 1 wherein said hard mineral particles have an average particle size in the range of about 20 to 40 micrometers.

9. The decorative laminate of claim 1 wherein said laminate is a high pressure decorative laminate.
- 5 10. The decorative laminate of claim 1 wherein said laminate is a low pressure decorative laminate.
11. The decorative laminate of claim 1 wherein the particle size distribution of said hard mineral particles comprises hard mineral particles having a first average particle size and hard mineral particles having at least one other average particle size.
- 10 12. The decorative laminate of claim 1 further including an overlay sheet interposed between the decorative surface and the hard mineral particles.
- 15 13. A laminate comprising:
- a. a base layer of cellulose fiber based material having a bottom surface and a top surface;
  - b. a first thermoset resin impregnating said cellulose fiber based material;
  - c. a second thermoset resin overcoated on said top surface of said base layer; and
  - 20 d. sufficient hard mineral particles distributed over said top surface of said base layer in said second thermoset resin of said laminate to improve wear resistance in said top surface, wherein at least a portion of said hard mineral particles comprise sol gel alpha alumina-based ceramic particles.
- 25 14. The laminate of claim 13 wherein said sol gel alpha alumina-based ceramic particles comprise up to 100% by weight of said hard mineral particles.
15. The laminate of claim 13 wherein said hard mineral particles have an average particle size in the range of about 5 to 70 micrometers.
- 30 16. The laminate of claim 13 wherein said laminate is a high pressure laminate.

17. The laminate of claim 13 wherein said laminate is a low pressure laminate.

18. The decorative laminate of claim 1 wherein the first and the second thermoset resins have the same composition.

5

19. The laminate of claim 13 wherein the first and the second thermoset resins have the same composition.

## INTERNATIONAL SEARCH REPORT

Inter national Application No  
PCT/US 01/28140

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/04 B32B29/06 B44C5/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B44C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE 199 33 710 A (CASALINI DANIELE) 25 January 2001 (2001-01-25) page 2; claims 1,4,19,20	1-5,7-19
X	US 4 880 689 A (RICHARDSON CALVIN ET AL) 14 November 1989 (1989-11-14) page 1	1-12
A	column 6, line 53-56 column 7, line 39 -column 8, line 50	13-19
X	US 5 928 778 A (KOBAYASHI TOSHITAKE ET AL) 27 July 1999 (1999-07-27) column 1, line 5-11 column 1, line 45 -column 4, line 52 column 10, line 57 -column 11, line 63	13-17,19
A		1-12,18
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

19 February 2002

Date of mailing of the international search report

28/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Ibarrola Torres, O



## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 01/28140

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 875 399 A (KAINDL M) 4 November 1998 (1998-11-04) page 3, line 34 - line 40; claims 1,6-9	1,3-5, 7-12
X	GB 1 433 464 A (FORMICA INT) 28 April 1976 (1976-04-28)  column 3, line 9,10; claims	1,4,5, 7-10, 12-19
A	WO 00 52105 A (SCARLETTE TERRY LANE) 8 September 2000 (2000-09-08) cited in the application page 1, line 10 -page 2, line 4	1-19

## INTERNATIONAL SEARCH REPORT

 Inter al Application No  
 PCT/US 01/28140

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 19933710	A	25-01-2001	DE 19933710 A1 EP 1070688 A1 JP 2001062961 A	25-01-2001 24-01-2001 13-03-2001
US 4880689	A	14-11-1989	AT 73056 T AU 605113 B2 AU 6415986 A BR 8605050 A CA 1278246 A1 DE 3684087 D1 EP 0219769 A2 ES 2030654 T3 MX 160128 A NZ 217751 A ZA 8607902 A	15-03-1992 10-01-1991 30-04-1987 14-07-1987 27-12-1990 09-04-1992 29-04-1987 16-11-1992 06-12-1989 26-02-1990 29-07-1987
US 5928778	A	27-07-1999	JP 2740943 B2 JP 8183147 A AU 710878 B2 AU 4321496 A CA 2180158 A1 CN 1142212 A ,B EP 0737567 A1 WO 9613381 A1 US 6040044 A NZ 286475 A	15-04-1998 16-07-1996 30-09-1999 23-05-1996 09-05-1996 05-02-1997 16-10-1996 09-05-1996 21-03-2000 28-01-1999
EP 0875399	A	04-11-1998	AT 405265 B AT 75297 A CZ 9801218 A3 DE 59801676 D1 DK 875399 T3 EP 0875399 A2 HU 9800937 A2 PL 326102 A1	25-06-1999 15-11-1998 11-11-1998 15-11-2001 04-02-2002 04-11-1998 30-11-1998 09-11-1998
GB 1433464	A	28-04-1976	AR 206622 A1 AU 7876875 A BR 7501259 A CA 1021130 A1 DE 2509338 A1 ES 435278 A2 FR 2263105 A1 IT 1046196 B ZA 7501313 A	06-08-1976 09-09-1976 02-12-1975 22-11-1977 11-09-1975 01-05-1977 03-10-1975 30-06-1980 28-01-1976
WO 0052105	A	08-09-2000	AU 3722500 A BR 0008653 A EP 1161503 A1 WO 0052105 A1	21-09-2000 18-12-2001 12-12-2001 08-09-2000